$$Ni(s) + 1/2O_2(g) \rightleftharpoons NiO(s) \tag{1}$$

$$H_2(g) + 1/2O_2(g) \rightleftharpoons H_2O(g) \tag{2}$$

And these reactions can be combined into a single equation.

$$Ni(s) + H_2O(g) \rightleftharpoons NiO(s) + H_2(g) \tag{3}$$

5 As can be seen from equation (3), the equilibrium of nickel catalyst oxidation is independent of pressure.

The corresponding equilibrium constants for reactions (1) and (2), respectively, are:

$$K_1 = \frac{a_{NiO}}{a_{Ni}\sqrt{a_{O_2}}} \tag{4}$$

$$K_2 = \frac{a_{H_2O}}{a_{H_2}\sqrt{a_{O_2}}} \tag{5}$$

10 where a_i are the individual activities of the reactants.

The equilibrium constants depend only on temperature and are available from the literature. In the temperature range of interest (400 °C – 900 °C), they can be approximated as follows.

$$K_1(T) = e^{(28,339K/T-10.345)} \tag{6}$$

and

15

$$K_2(T) = e^{(29,607K/T-6.408)} \tag{7}$$

4

To determine whether nickel oxide formation occurs during steam purging, the activity of NiO needs to be calculated. To do so, equilibrium calculations are

$$a_{NiO} = K_1\sqrt{a_{O_2}} \tag{8}$$

performed based on the initial assumption that nickel in the catalyst is stable, i.e., the activity of Ni(s) is equal to 1. Then, equation (4) can be rewritten.

5   If the calculated activity of NiO is less than 1, then the initial assumption is correct and NiO formation does not occur. If the calculated activity of NiO is equal to 1, both solid phases will coexist, and some oxidation of the nickel will occur. If the calculated activity of NiO is greater than 1, the assumption that Ni(s) is stable is no longer true. Under conditions where the activity of NiO is greater than 1, Ni(s) will be oxidized to

10   NiO.

In order to calculate the activity of NiO, it follows from equation (8) that the activity of oxygen must be determined. The relationship between the activities of the gaseous reactants and their mole fractions, assuming ideal gas behavior, is given by the equation:

$$a_i = x_i \frac{p}{p^0} \tag{9}$$

15

where x_i is the mole fraction of the reactant, p is pressure, and p^0 is the reference pressure.

Hence, equation (5) can be rewritten as

$$K_2 = \frac{x_{H_2O}}{x_{H_2}\sqrt{a_{O_2}}} \tag{10}$$

Where the purge gas is pure steam, the mole fraction of steam approaches 1.

20

$$x_{H_2O} \approx 1 \tag{11}$$

Any oxygen and hydrogen present come from the dissociation of the steam, and the following relationship applies.

$$X_{H_2} = 2X_{O_2} \tag{12}$$

Substituting into equation (10) yields the following equation for the oxygen activity at $p = p^0$.

$$a_{O_2} = \left(\frac{1}{2K_2}\right)^{2/3} \tag{13}$$

5   At temperatures between 400 °C and 900 °C, the activity of NiO calculated from equations (13), (8) and (7) is several orders of magnitude greater than 1. Accordingly, the nickel catalyst in a steam reformer will be oxidized by a pure steam purge.

       Figure 1 illustrates the temperature dependency of equilibrium constants K_1 and K_2 in the temperature range of 400 °C to 900 °C (673 K to 1173 K). Figure 1 is a plot

10   of ln K, as calculated from equations (6) and (7), respectively, against 1/T.

       As indicated in Figure 1, K_2 is larger than K_1 over the normal operating temperature range of steam reformers. Thus, during purging at these temperatures, the formation of steam is favored over formation of NiO. In other words, the affinity of hydrogen for oxygen is greater than the affinity of nickel for oxygen. This suggests that

15   hydrogen acts as an efficient oxygen scavenger under such conditions.

       Assuming a suitable excess of hydrogen, oxygen should be consumed by the hydrogen, thus protecting the nickel in the catalyst from oxidation. In this case, the mole fraction balance of gas in the reformer is

$$X_{H_2} + X_{H_2O} = 1 \tag{14}$$

20   And equation (10) can be rewritten.

$$K_2 = \frac{(1 - X_{H_2})}{X_{H_2}\sqrt{a_{O_2}}} \tag{15}$$

6